



(12) **United States Patent**
Jiang et al.

(10) **Patent No.:** **US 9,107,308 B2**
(45) **Date of Patent:** **Aug. 11, 2015**

- (54) **GRAPHITIC SUBSTRATES WITH CERAMIC DIELECTRIC LAYERS**
(71) Applicants: **Nan Jiang**, Austin, TX (US); **Zvi Yaniv**, Austin, TX (US)
(72) Inventors: **Nan Jiang**, Austin, TX (US); **Zvi Yaniv**, Austin, TX (US)
(73) Assignee: **PEN Inc.**, Deerfield Beach, FL (US)
(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

- (21) Appl. No.: **14/380,981**
(22) PCT Filed: **Feb. 26, 2013**
(86) PCT No.: **PCT/US2013/027717**
§ 371 (c)(1),
(2) Date: **Aug. 26, 2014**

- (87) PCT Pub. No.: **WO2013/130418**
PCT Pub. Date: **Sep. 6, 2013**

- (65) **Prior Publication Data**
US 2015/0047882 A1 Feb. 19, 2015

- Related U.S. Application Data**
(60) Provisional application No. 61/603,479, filed on Feb. 27, 2012.
(51) **Int. Cl.**
H05K 1/03 (2006.01)
H05K 1/05 (2006.01)
(Continued)
(52) **U.S. Cl.**
CPC **H05K 1/053** (2013.01); **C04B 41/009** (2013.01); **C04B 41/52** (2013.01); **C04B 41/90** (2013.01); **H05K 1/0284** (2013.01); **H05K 1/09** (2013.01); **H05K 3/12** (2013.01);
(Continued)

- (58) **Field of Classification Search**
CPC H05K 1/00; H05K 1/18; H05K 1/053; H05K 1/056; H05K 3/10; H01L 23/142; H01L 23/3736; H01L 31/02; H01L 31/068; H01L 31/0224; H01M 8/02; H01M 8/10; H01M 8/24
See application file for complete search history.

- (56) **References Cited**
U.S. PATENT DOCUMENTS
5,841,608 A * 11/1998 Kasamatsu et al. 360/236.6
6,020,083 A * 2/2000 Breault et al. 429/492
(Continued)

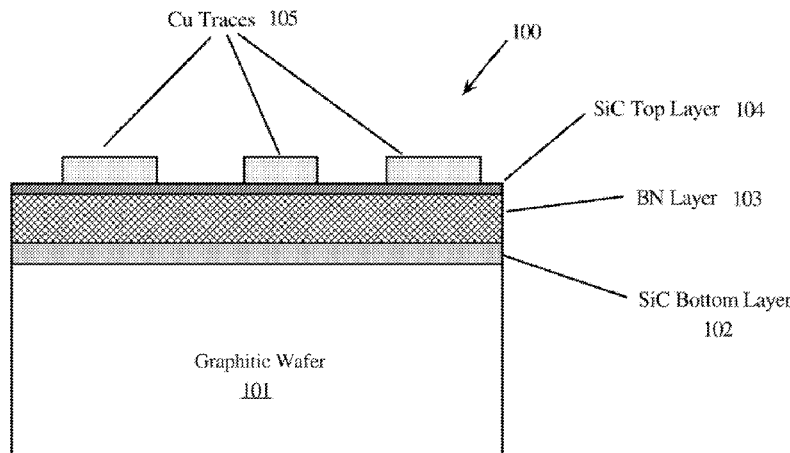
- FOREIGN PATENT DOCUMENTS**
EA 008748 B1 8/2007
EP 0790762 B1 10/2003
(Continued)
OTHER PUBLICATIONS

International Bureau of WIPO, International Preliminary Report on Patentability, International Application No. PCT/2013/027717, dated Sep. 12, 2014.
Russian Federation International Searching Authority; International Search Report & Written Opinion for PCT/US2013/027717; May 23, 2013; Moscow, RU.

Primary Examiner — Xiaoliang Chen
(74) *Attorney, Agent, or Firm* — Kelly Kordzik; Matheson Keys & Kordzik PLLC

- (57) **ABSTRACT**
Different kinds of printing pastes or inks are utilized in various combinations to develop multiple ceramic dielectric layers on graphitic substrates in order to create effective dielectric ceramic layers that combine good adhesion to both graphitic substrates and printed copper traces, and strong insulating capability. The pastes or inks may comprise a high thermal conductivity powder.

14 Claims, 8 Drawing Sheets



(51) **Int. Cl.**

C04B 41/90 (2006.01)
C04B 41/00 (2006.01)
C04B 41/52 (2006.01)
H05K 1/02 (2006.01)
H05K 1/09 (2006.01)
H05K 3/12 (2006.01)
H01L 23/373 (2006.01)
H05K 1/18 (2006.01)
C04B 111/00 (2006.01)

(52) **U.S. Cl.**

CPC *C04B 2111/00844* (2013.01); *H01L 23/373*
 (2013.01); *H01L 2924/0002* (2013.01); *H05K*
1/181 (2013.01); *H05K 2201/0104* (2013.01);
H05K 2201/0137 (2013.01); *H05K 2201/0195*
 (2013.01); *H05K 2201/0323* (2013.01); *H05K*
2201/06 (2013.01); *H05K 2201/10106*
 (2013.01)

(56)

References Cited

U.S. PATENT DOCUMENTS

6,025,062	A *	2/2000	Krenkel et al.	428/293.4
6,301,079	B1 *	10/2001	Hanamoto et al.	360/236.5
7,303,005	B2	12/2007	Reis et al.	
2006/0101860	A1 *	5/2006	Chen	65/374.11
2006/0269753	A1 *	11/2006	Peng et al.	428/408
2007/0212567	A1 *	9/2007	Esaki et al.	428/650
2011/0001418	A1 *	1/2011	Tsai	313/46
2011/0041903	A1 *	2/2011	Zehavi et al.	136/255
2012/0298408	A1 *	11/2012	Nagatomo et al.	174/260

FOREIGN PATENT DOCUMENTS

RU	2256307	C2	7/2005
RU	92568	U1	3/2010
RU	2411609	C1	2/2011

* cited by examiner

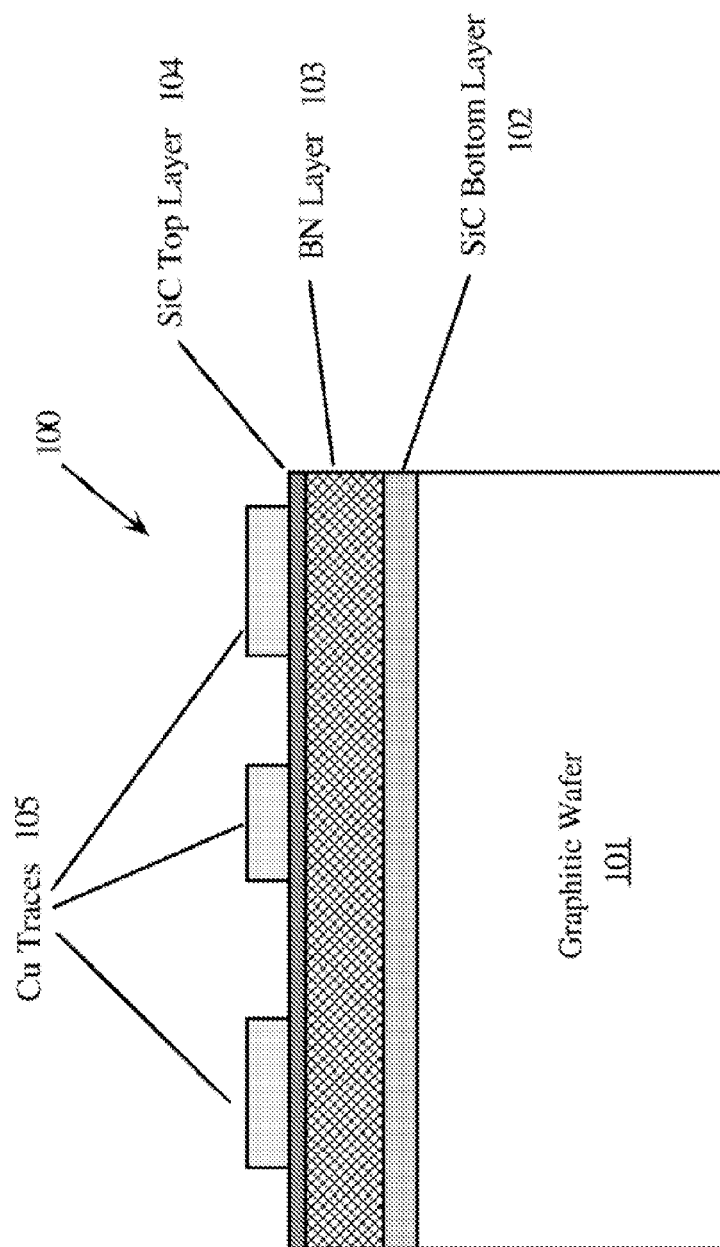


FIG. 1

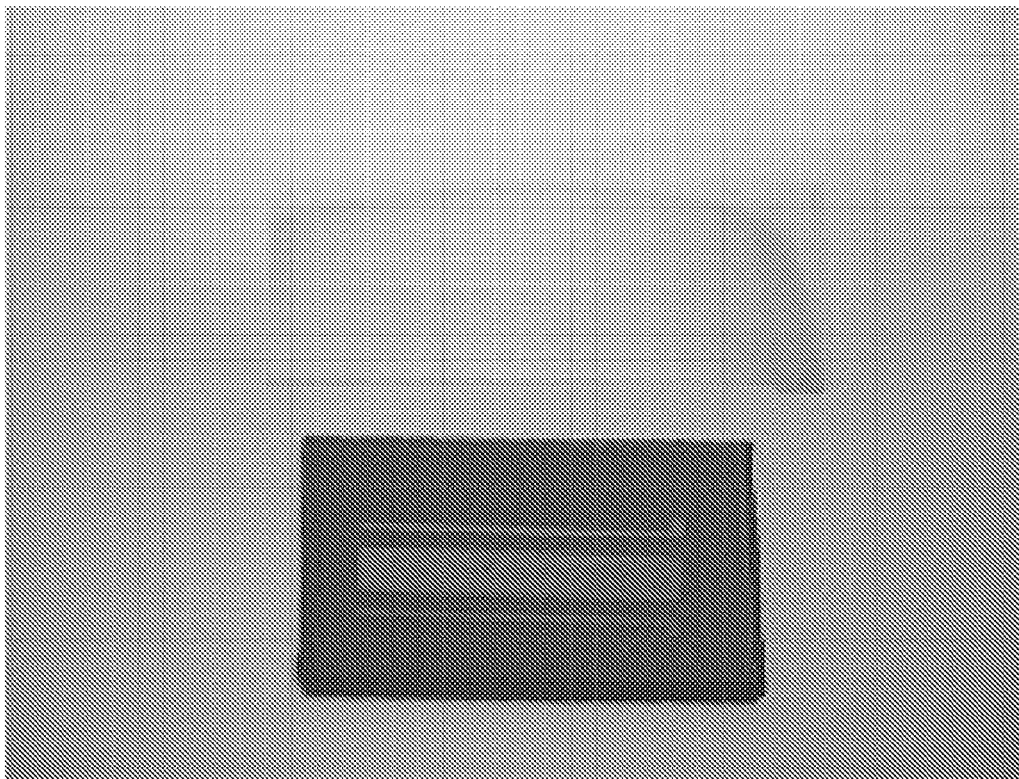


FIG. 2

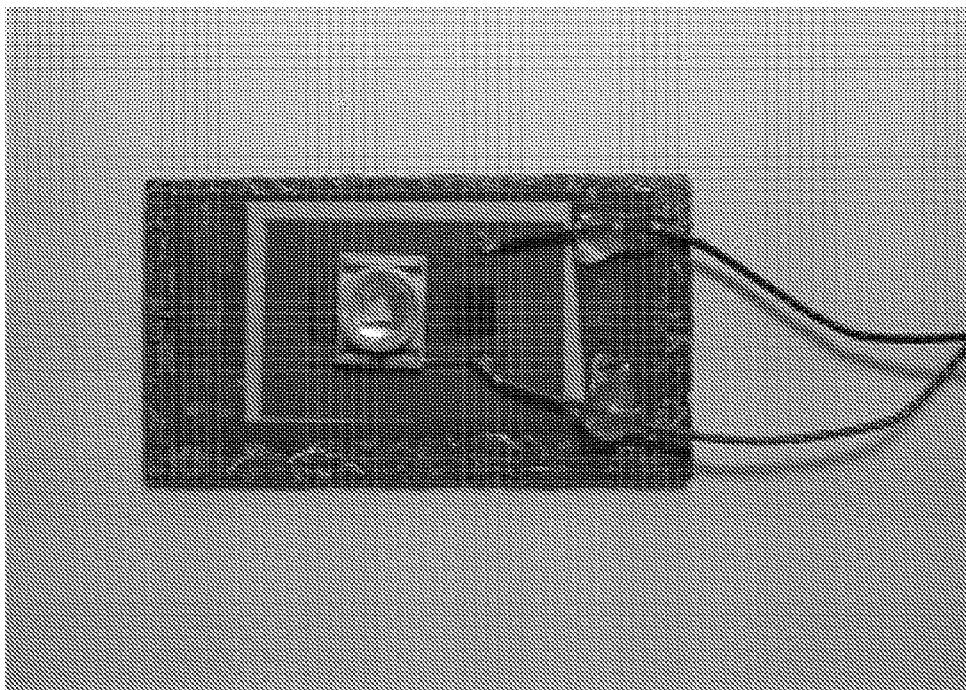


FIG. 3A

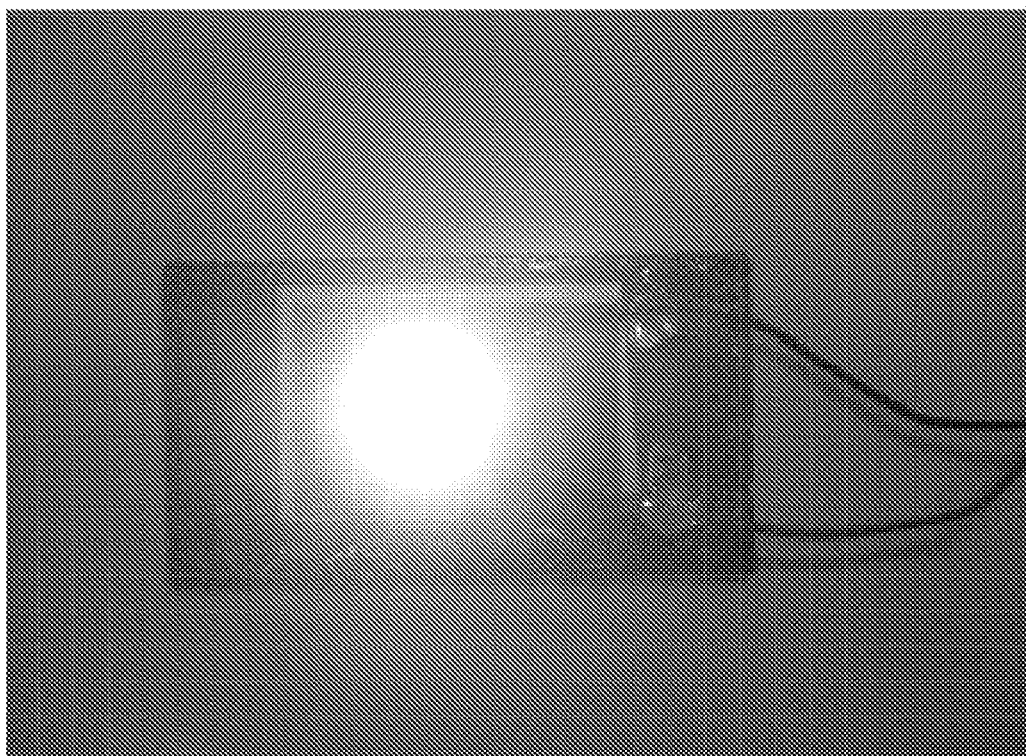


FIG. 3B

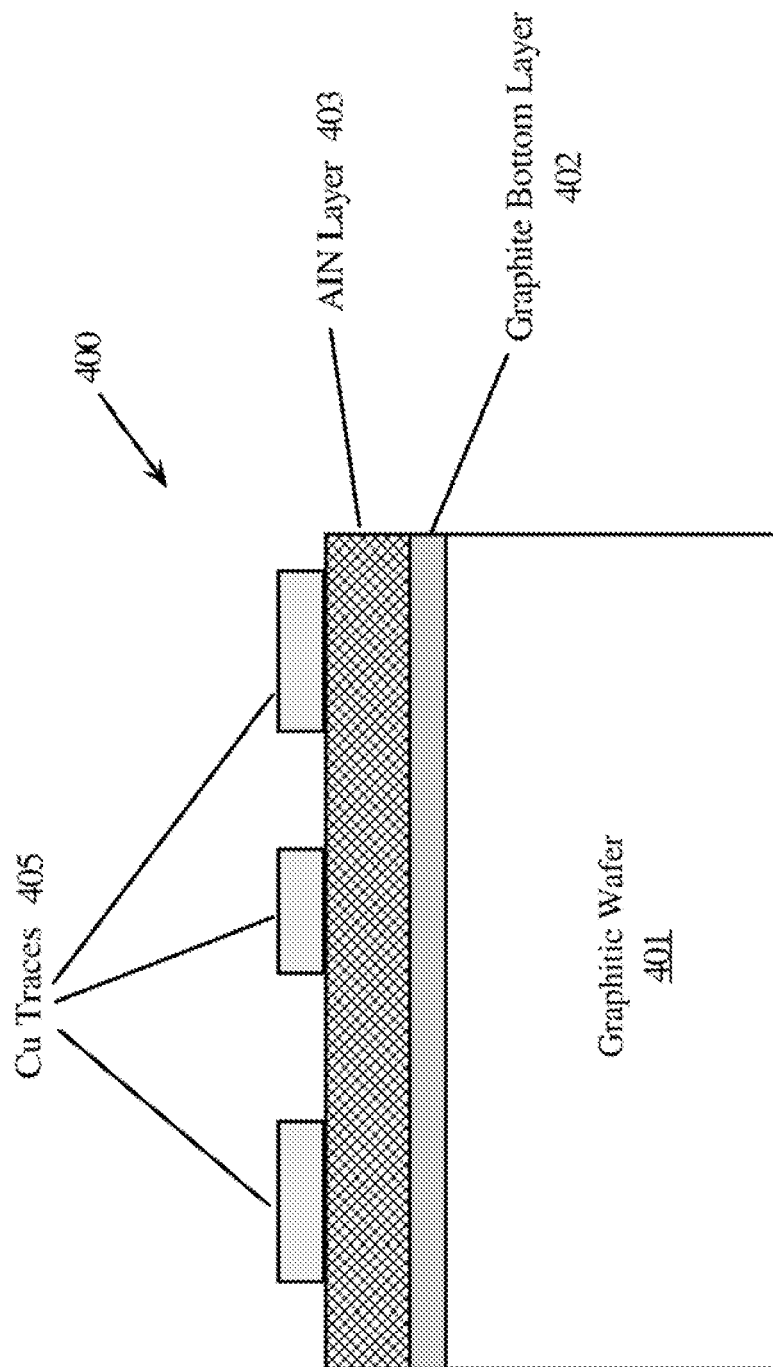


FIG. 4

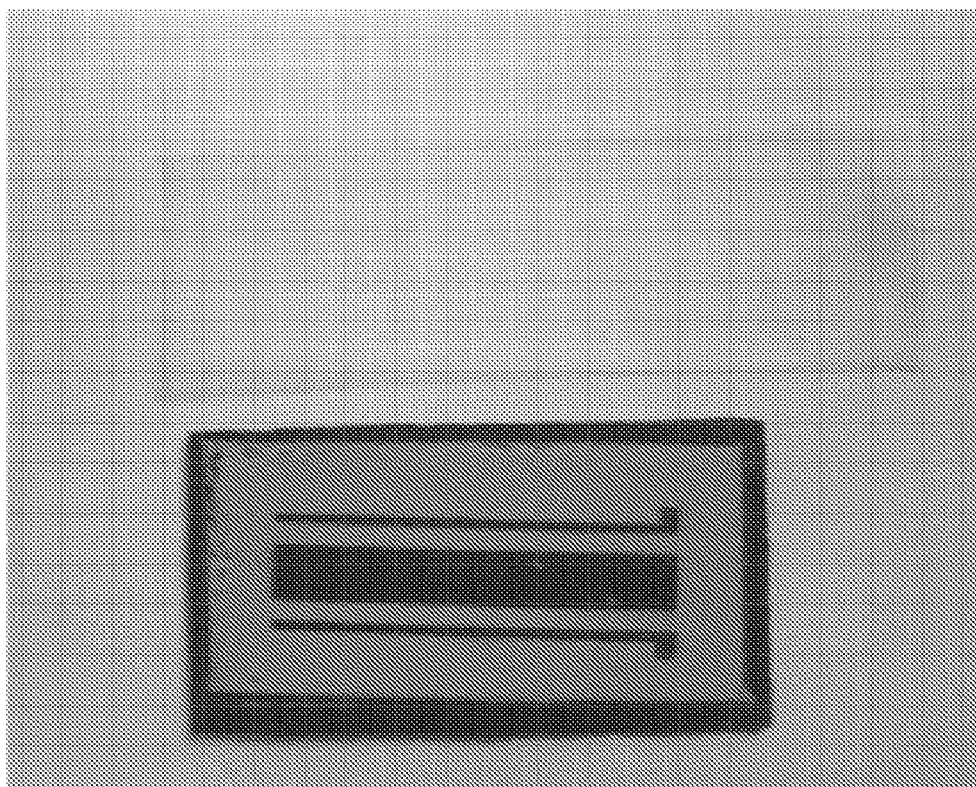


FIG. 5A

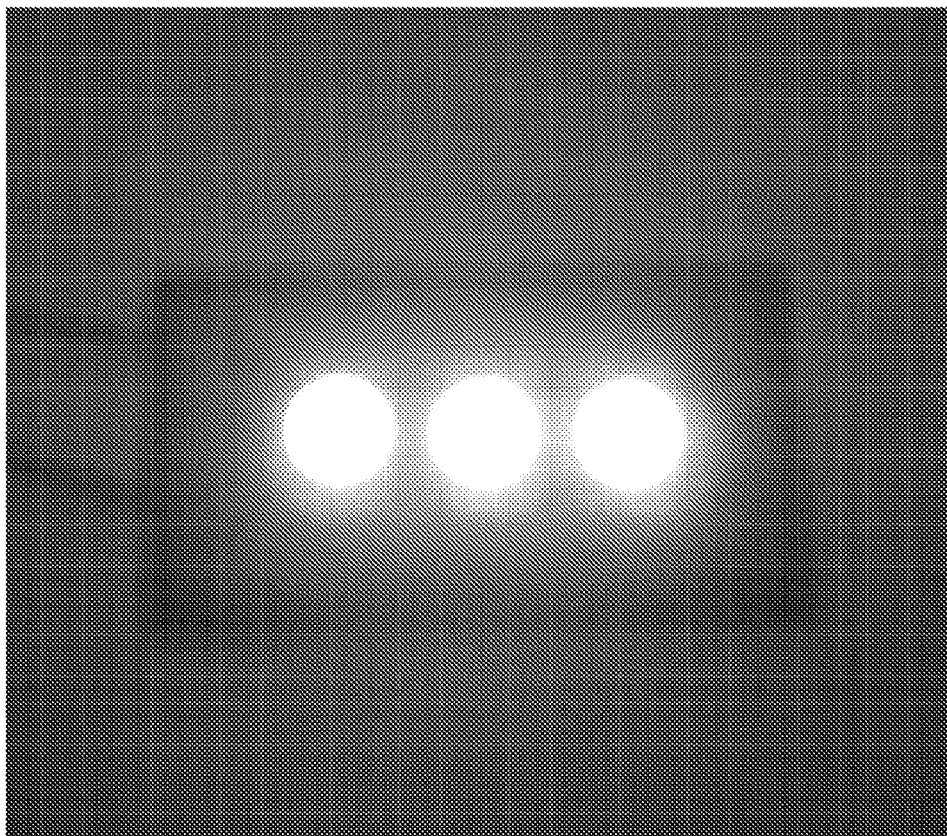


FIG. 5B

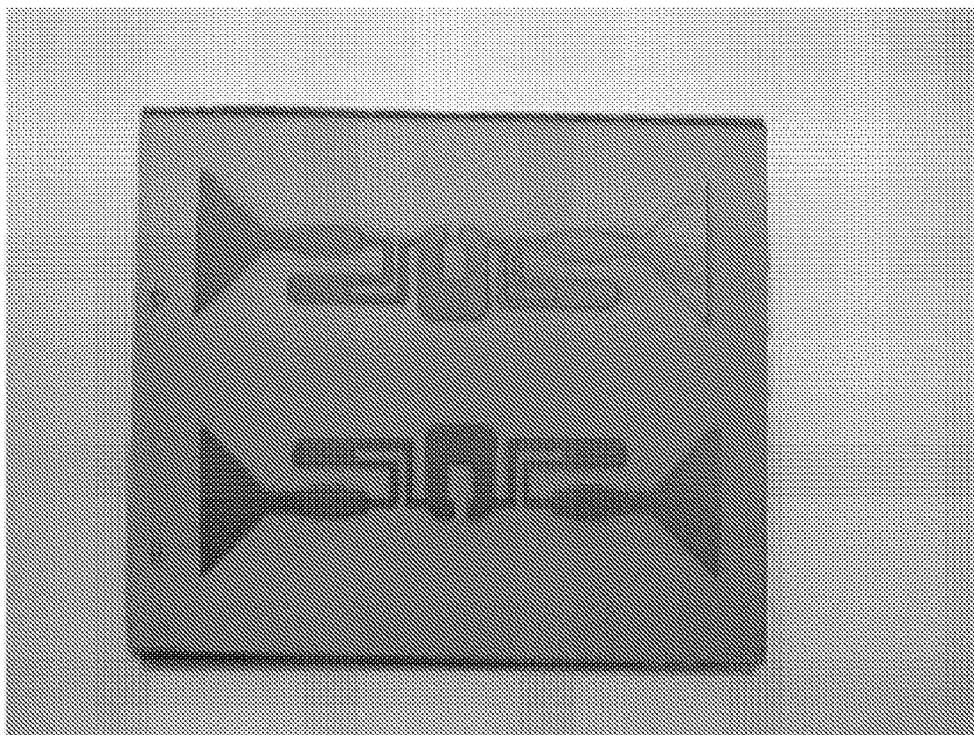


FIG. 6

1

GRAPHITIC SUBSTRATES WITH CERAMIC DIELECTRIC LAYERS

This application claims priority to U.S. Provisional Application Ser. No. 61/603,479, which is hereby incorporated by reference herein.

TECHNICAL FIELD

This application relates in general to electronic circuitry, and in particular, to conductivity of heat in electronic circuitry.

BACKGROUND INFORMATION

Thermal management materials with high thermal conductivity, high thermal diffusivity, machineability and low coefficient of thermal expansion ("CTE") at low cost are desirable. For many electronic applications it would be beneficial if the material was not electrically conductive so that electronic components could be assembled directly onto the high thermal conductivity material. However, materials with high thermal conductivity are also typically electrically conductive. For example, carbon-based materials, such as graphite and graphene, typically have high thermal conductivity and are also electrically conductive. It would be desirable to have high thermal conductivity ceramic dielectric layers on graphitic substrates (i.e., a pure graphite substrate or a graphite-metal composite substrate) for fabrication of a high-performance circuit board through printing copper ("Cu") circuit traces on the top of the ceramic dielectric layers.

Besides providing high thermal performance and sufficient dielectric strength, the dielectric layers should also possess a strong, adhesion with graphitic substrates, be compatible with Cu paste printing and curing processes that require a curing temperature over 400° C., and possess a strong adhesion with the Cu printed circuit traces.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates an embodiment of the present invention;

2

FIG. 2 illustrates a digital image of copper traces printed on a wafer structure as illustrated in FIG. 1, showing that there is not any delamination after a taping test;

FIGS. 3A-3B show digital images of a circuit board configured with a wafer structure as illustrated in FIG. 1 with an LED soldered thereon;

FIG. 4 illustrates an embodiment of the present invention;

FIGS. 5A-5B show digital images of a circuit board configured in accordance with the embodiment illustrated in FIG. 4 with LEDs soldered thereon; and

FIG. 6 shows a digital image of a RFID circuit board configured with a wafer structure in accordance with the embodiment illustrated in FIG. 4, with a size of 85 mm×70 mm.

DETAILED DESCRIPTION

In order to create effective dielectric ceramic layers that combine good adhesion to both graphitic substrates and printed Cu, and strong insulating capability, multiple ceramic layer structures on graphitic substrates are implemented in embodiments of the present invention.

Generally, compared with polymeric dielectric layers (e.g., epoxy, silicone, polyimide), ceramic-type dielectric layers (e.g., made with ceramic powders, such as aluminum nitride ("AlN"), boron nitride ("BN"), silicon carbide ("SiC"), etc.) have much higher thermal conductivity and a lower CTE that matches well with typical semiconductor materials (e.g., Si, GaN, GaAs).

In embodiments of the present invention, different kinds of printing pastes or inks are utilized in various combinations, some of which are more specifically described herein, to develop multiple ceramic dielectric layers on graphitic substrates. The pastes or inks may comprise a high thermal conductivity powder (e.g., AlN, BN, SiC, or graphite micron powders) and a nonorganic binder. Water may be used as a vehicle to adjust the viscosity. The pastes or inks are further described in Table 1.

TABLE 1

	Composition	Advantages	Disadvantages
AlN paste or ink	AlN powders + Lithium polysilicate binder + vehicle (e.g., water)	Good adhesion to printed Cu traces (no delamination occurred during the taping test). Intrinsically had good thermal conductivity and insulating properties.	Poor adhesion to graphitic substrate (delamination occurred during the taping test).
BN paste or ink	BN powders + monoaluminum phosphate binder + vehicle (e.g., water)	Intrinsically had good thermal conductivity and insulating properties	Poor adhesion to both graphitic substrate and Cu traces (delamination occurred during the taping test).
SiC paste or ink	SiC powders + monoaluminum phosphate binder + vehicle (e.g., water)	Good adhesion to both graphitic substrate and Cu printed traces (no delamination occurred during the taping test). Intrinsically had good thermal conductivity.	Weak insulating capability (i.e., a weak electrically insulating capability)
Graphite paste or ink	Graphite powders with Al ₂ O ₃ addition + silicate binder + vehicle (e.g., water)	Good adhesion to graphitic substrate (no delamination occurred during the taping test). Intrinsically had a good thermal conductivity.	Reacted with Cu printed traces during Cu curing process. Electrically conductive material and cannot be used as the sole insulating layer.

3

A SiC/BN/SiC/Graphitic-wafer structure **100** in accordance with embodiments of the present invention is illustrated in cross-section in FIG. 1. As indicated in Table 1, the bottom SiC layer **102**, possesses a strong adhesion to the graphitic wafer **101**, the middle BN layer **103** offers sufficient electrical insulating strength, and the top SiC layer **104** enhances the adhesion to the Cu traces **105**. Each of the layers **102-105** may be deposited by ink or paste printing or spraying techniques well known in the art.

FIG. 2 shows a LED circuit board made according to this SiC/BN/SiC/Graphitic-wafer design **100**. From FIG. 2, it can be seen for both the ceramic layers and Cu traces, no delamination occurs after a taping test (an adhesive tape is pressed on the layer or trace and pulled off; no peeled off Cu or ceramic fragments were left on the tape), indicating a good adhesion strength of this structure.

The Cu traces **105** on the ceramic dielectric layer are configured to be solderable. As shown in FIGS. 3A-3B, a chip can be tightly soldered onto the Cu traces (e.g., using lead-free tin solder). FIG. 3B shows that the structure was successful by the activation of the LED. Note that the lighter colored layer in FIGS. 3A-3B is the middle BN layer **103**.

An AlN/Graphite/Graphitic-wafer structure **400** in accordance with embodiments of the present invention is illustrated in cross-section in FIG. 4. The bottom graphite layer **402** may be printed or sprayed on the graphitic wafer **401**. Using a diluted graphite paste may provide, a stronger adhesion to the graphitic wafer. The AlN layer **403** may be printed or sprayed onto the graphite layer **402**. The copper ("Cu") traces **405** may be printed or sprayed onto the AlN layer **403**.

FIGS. 5A-5B show a LED circuit board manufactured based on the foregoing AlN/Graphite/Graphitic-wafer **400**. No delamination occurred after a taping test, and also the LED chips can be tightly soldered onto the Cu traces **405**. FIG. 5B shows that the structure assembly was successful by the activation of the LEDs.

FIG. 6 shows a RFID circuit board built on an AlN/Graphite/Graphitic-wafer substrate **400**, wherein two RFID patterned circuits **405** were printed on the top of the AlN layer **403**.

What is claimed is:

1. A structure for electrical circuitry comprising: electrically conducting traces; a graphitic substrate; and a plurality of layers separating the electrically conducting traces from the graphitic substrate, wherein the plurality of layers are selected from the group consisting of:
 - (i) a plurality of different ceramic dielectric layers,
 - (ii) a graphitic layer and a ceramic dielectric layer, and
 - (iii) a graphitic layer and two or more different ceramic dielectric layers,
 wherein the plurality of layers are a first silicon carbide layer deposited onto the graphitic substrate, a boron nitride layer deposited onto the first silicon carbide layer, and a second silicon carbide layer deposited onto the boron nitride layer, wherein the electrically conducting traces are deposited onto the second silicon carbide layer.
2. The structure as recited in claim 1, wherein the electrically conducting traces comprise copper.
3. A structure for electrical circuitry comprising: electrically conducting traces; a graphitic substrate; and a plurality of layers separating the electrically conducting traces from the graphitic substrate, wherein the plurality of layers are selected from the group consisting of:

4

- (i) a plurality of different ceramic dielectric layers,
 - (ii) a graphitic layer and a ceramic dielectric layer, and
 - (iii) a graphitic layer and two or more different ceramic dielectric layers,
 wherein the plurality of layers are a graphite layer deposited onto the graphitic substrate, and an aluminum nitride layer deposited onto the graphite layer, wherein the electrically conducting traces are deposited onto the aluminum nitride layer.
4. The structure as recited in claim 3, wherein the electrically conducting traces comprise copper.
5. A structure for electrical circuitry comprising: electrically conducting traces; a graphitic substrate; and a plurality of layers separating the electrically conducting traces from the graphitic substrate, wherein the plurality of layers are selected from the group consisting of:
 - (i) a plurality of different ceramic dielectric layers,
 - (ii) a graphitic layer and a ceramic dielectric layer, and
 - (iii) a graphitic layer and two or more different ceramic dielectric layers,
 wherein the plurality of different ceramic dielectric layers comprise a first silicon carbide layer deposited onto the graphitic substrate, a boron nitride layer deposited onto the first silicon carbide layer, and a second silicon carbide layer deposited onto the boron nitride layer, wherein the electrically conducting traces are deposited onto the second silicon carbide layer.
6. The structure as recited in claim 5, wherein the electrically conducting traces comprise copper.
7. A structure for electrical circuitry comprising: electrically conducting traces; a graphitic substrate; and a plurality of layers separating the electrically conducting traces from the graphitic substrate, wherein the plurality of layers are selected from the group consisting of:
 - (i) a plurality of different ceramic dielectric layers,
 - (ii) a graphitic layer and a ceramic dielectric layer, and
 - (iii) a graphitic layer and two or more different ceramic dielectric layers, wherein the graphite layer and the ceramic dielectric layer comprise the graphite layer deposited onto the graphitic substrate, and an aluminum nitride layer deposited onto the graphite layer, wherein the electrically conducting traces are deposited onto the aluminum nitride layer.
8. The structure as recited in claim 7, wherein the electrically conducting traces comprise copper.
9. A method of making electrical circuitry comprising: depositing a plurality of layers over a graphitic substrate, wherein the plurality of layers are selected from the group consisting of:
 - (i) a plurality of different ceramic dielectric layers,
 - (ii) a graphitic layer and a ceramic dielectric layer, and
 - (iii) a graphitic layer and two or more different ceramic dielectric layers; and
 depositing electrically conducting traces on a top one of the plurality of layers, wherein depositing of the plurality of layers over the graphitic substrate comprises depositing a first silicon carbide layer onto the graphitic substrate, depositing a boron nitride layer onto the first silicon carbide layer, and depositing a second silicon carbide layer onto the boron nitride layer, wherein the electrically conducting traces are deposited onto the second silicon carbide layer.
10. The method as recited in claim 9, wherein the electrically conducting traces comprise copper.

11. The method as recited in claim **10**, wherein the first and second silicon carbide layers are deposited as paste or ink formulations comprising silicon carbide powders, and wherein the boron nitride layer is deposited as a paste or ink formulation comprising boron nitride powders. 5

12. A method of making electrical circuitry comprising: depositing a plurality of layers over a graphitic substrate, wherein the plurality of layers are selected from the group consisting of:
 (i) a plurality of different ceramic dielectric layers, 10
 (ii) a graphitic layer and a ceramic dielectric layer, and
 (iii) a graphitic layer and two or more different ceramic dielectric layers; and

depositing electrically conducting traces on a top one of the plurality of layers, wherein 15
 depositing of the plurality of layers over the graphitic substrate comprises depositing a graphite layer onto the graphitic substrate, and depositing an aluminum nitride layer onto the graphite layer, wherein the electrically conducting traces are deposited onto the aluminum 20
 nitride layer.

13. The method as recited in claim **12**, wherein the electrically conducting traces comprise copper.

14. The method as recited in claim **13**, wherein the aluminum nitride layer is deposited as a paste or ink formulation 25
 comprising aluminum nitride powders, and
 wherein the graphite layer is deposited as a paste or ink formulation comprising graphite powders.

* * * * *